

## DESCRIPTION

### PIEZOELECTRIC CERAMIC AND METHOD OF MANUFACTURIGN THE SAME

#### TECHNICAL FIELD

The present invention relates to a piezoelectric ceramic including a composition including a perovskite-type oxide and a tungsten bronze-type oxide, and being suitable for vibration devices such as actuators, sound components, sensors and so on, and a method of manufacturing the same.

#### BACKGROUND ART

An actuator using a piezoelectric ceramic uses a piezoelectric effect in which the application of an electric field generates mechanical strain and stress. The actuator has characteristics such as the capability of obtaining a very small displacement with high accuracy, and large strain, and, for example, the actuator is used to position a precision tool or an optical device. As a conventional piezoelectric ceramic used for actuators, lead zirconate titanate (PZT) having excellent piezoelectric properties is most commonly used. However, lead zirconate titanate includes a large amount of lead, so adverse effects on global environment such as leaching of lead caused by acid rain have become issues recently. Therefore, the development of piezoelectric ceramics not including lead instead of lead zirconate titanate is desired.

As the piezoelectric ceramic not including lead, for example, a

piezoelectric ceramic including barium titanate ( $\text{BaTiO}_3$ ) as a main component is known (refer to Japanese Unexamined Patent Application Publication No. H2-159079). The piezoelectric ceramic is superior in a relative dielectric constant  $\epsilon_r$  and a electromechanical coupling factor  $k_r$ , so the piezoelectric ceramic holds promise as a piezoelectric material for actuators. Moreover, as another piezoelectric ceramic not including lead, for example, a piezoelectric ceramic including sodium lithium potassium niobate as a main component is known (refer to Japanese Unexamined Patent Application Publication No. S49-125900 or Japanese Examined Patent Publication No. S57-6713). The piezoelectric ceramic has a high Curie temperature of 350°C or over, and an excellent electromechanical coupling factor  $k_r$ , so the piezoelectric ceramic holds promise as a piezoelectric material. Further, a compound including potassium sodium niobate and a tungsten bronze-type oxide has been recently reported (Japanese Unexamined Patent Application Publication No. H9-165262).

However, the piezoelectric ceramics not including lead have such an issue that they have lower piezoelectric properties, compared to lead-based piezoelectric ceramics, thereby a sufficiently large amount of displacement cannot be obtained. Moreover, in the piezoelectric ceramic including sodium lithium potassium niobate as a main component, sodium, potassium and lithium are easily volatilized during sintering, so there is such an issue that sintering is difficult.

#### DISCLOSURE OF THE INVENTION

In view of the foregoing, it is an object of the invention to provide a piezoelectric ceramic being capable of obtaining a large amount of displacement, and being easily sintered, and being superior in the point of low emission, environment and ecology, and a method of manufacturing the same.

A piezoelectric ceramic according to the invention includes: a composition including a first perovskite-type oxide, a second perovskite-type oxide and a tungsten bronze-type oxide, wherein the first perovskite-type oxide includes a first element including sodium (Na) and potassium (K), a second element including at least niobium (Nb) selected from the group consisting of niobium and tantalum (Ta), and oxygen (O), the second perovskite-type oxide includes a third element including an alkaline-earth metal element, a fourth element including zirconium (Zr), and oxygen, and the content of the second perovskite-type oxide in the composition is less than 10 mol%.

The content of potassium in the first element is preferably within a range from 10 mol% to 90 mol% inclusive. The first element preferably further includes lithium, and the content of lithium in the first element is preferably 10 mol% or less.

Moreover, the content of the tungsten bronze-type oxide in the composition is preferably 1 mol% or less. The tungsten bronze-type oxide preferably includes a fifth element including an alkaline-earth metal element, a sixth element including at least niobium selected from the group consisting of niobium and tantalum, and oxygen.

Further, the total content of tantalum in the second element and the sixth element is preferably within a range from 0 mol% to 10 mol% inclusive.

In addition, the composition is considered as a main component, and as a sub-component, at least one kind selected from the group consisting of elements of Groups 3 through 14 in the long form of the periodic table of the elements, more specifically manganese (Mn) is preferably included, and in addition to manganese, at least one kind selected from the group consisting of cobalt (Co), iron (Fe), nickel (Ni), zinc (Zn), scandium (Sc), titanium (Ti), zirconium (Zr), hafnium (Hf), aluminum (Al), gallium (Ga), indium (In), silicon (Si), germanium (Ge) and tin (Sn) is more preferably included.

A method of manufacturing a piezoelectric ceramic according to the invention, the piezoelectric ceramic including a first perovskite-type oxide, a second perovskite-type oxide and a tungsten bronze-type oxide, the first perovskite-type oxide including a first element including sodium (Na) and potassium (K), a second element including at least niobium (Nb) selected from the group consisting of niobium and tantalum (Ta) and oxygen (O), the second perovskite-type oxide including a third element including at least one kind selected from alkaline-earth metal elements, a fourth element including zirconium (Zr) and oxygen, the method includes the step of calcining a mixture including elements of the first perovskite-type oxide, the second perovskite-type oxide, and elements of the tungsten bronze-type oxide.

In the piezoelectric ceramic according to the invention, the first perovskite-type oxide including sodium, potassium and niobium, the second perovskite-type oxide including an alkaline-earth metal element and zirconium, and the tungsten bronze-type oxide are included, and the content of the second perovskite-type oxide in the main component is less than 10 mol%, so the amount of displacement can be increased. Moreover, sintering can be easily performed. Therefore, availability of the piezoelectric ceramic and the piezoelectric device including no lead or a smaller content of lead can be increased. In other words, the volatilization of lead during sintering is reduced, and the risk of emitting lead into environment is lower even after the piezoelectric ceramic and the piezoelectric device are distributed in a market and then disposed, so the piezoelectric ceramic and the piezoelectric device being superior in the point of low emission, environment and ecology can be utilized.

In particular, when the content of potassium in the first element is within a range from 10 mol% to 90 mol% inclusive, superior piezoelectric properties can be obtained, and sintering can be more easily performed.

Moreover, when the first element includes 10 mol% or less of lithium, the amount of displacement can be further increased.

Further, when the content of the tungsten bronze-type oxide in the composition is 1 mol% or less, the amount of displacement can be further increased.

In addition, when the tungsten bronze-type oxide includes the third element including an alkaline-earth metal element, the fourth element

including at least niobium selected from the group consisting of niobium and tantalum, and oxygen, superior piezoelectric properties can be obtained.

Furthermore, when the total content of tantalum in the second element and the sixth element is 10 mol% or less, the amount of displacement can be further increased.

In addition, when at least one kind selected from the group consisting of elements of Groups 3 through 14 in the long form of the periodic table of the elements is included as the sub-component, the piezoelectric properties can be further improved. In particular, when manganese as an oxide is included as the first sub-component within a range of 0.1 wt% to 1 wt% inclusive relative to the main component, the sinterability can be improved, thereby the piezoelectric properties can be improved. Further, when, in addition to manganese, at least one kind selected from the group consisting of cobalt, iron, nickel, zinc, scandium, titanium, zirconium, hafnium, aluminum, gallium, indium, silicon, germanium and tin as an oxide is included as a second sub-component within a range from 0.01 wt% to 1 wt% relative to the main component in total, the piezoelectric properties can be further improved.

Moreover, in the method of manufacturing a piezoelectric ceramic according to the invention, a mixture including elements of the first perovskite-type oxide, the second perovskite-type oxide, and elements of the tungsten bronze-type oxide is calcined, so the piezoelectric ceramic according to the invention can be easily obtained, and the piezoelectric

ceramic according to the invention can be achieved.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an illustration of a piezoelectric device using a piezoelectric ceramic according to an embodiment of the invention;

FIG. 2 is a flowchart showing a method of manufacturing the piezoelectric ceramic according to the embodiment of the invention and a piezoelectric device; and

FIG. 3 is an illustration of a displacement measuring device used for measuring the amount of displacement in examples of the invention.

#### BEST MODE FOR CARRYING OUT THE INVENTION

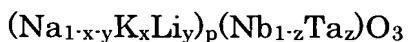
A preferred embodiment of the present invention will be described in more detail below.

A piezoelectric ceramic according to an embodiment of the invention includes a composition including a first perovskite-type oxide, a second perovskite-type oxide and a tungsten bronze-type oxide as a main component. In the composition, the first perovskite-type oxide, the second perovskite-type oxide and the tungsten bronze-type oxide may form a solid solution, or may not perfectly form a solid solution.

The first perovskite-type oxide includes a first element, a second element and oxygen. The first element includes at least sodium and potassium, and preferably further includes lithium. The second element includes at least niobium, and preferably further includes tantalum. It is

because in this case, superior piezoelectric properties can be obtained by including no lead or reducing the content of lead. Further, it is because the Curie temperature can be increased, thereby an operating temperature range can be extended. The chemical formula of the first perovskite-type oxide is represented by, for example, Chemical Formula 1.

[Chemical Formula 1]



In the formula, the values of x, y and z are within a range of  $0 < x < 1$ ,  $0 \leq y < 1$  and  $0 \leq z < 1$ , respectively. When the first perovskite-type oxide has a stoichiometric composition, p is 1, but the perovskite-type oxide may deviate from the stoichiometric composition. The composition of oxygen is stoichiometrically determined, and it may deviate from the stoichiometric composition.

The content of potassium in the first element is preferably within a range of 10 mol% to 90 mol% inclusive. In other words, for example, the value of x in Chemical Formula 1 is preferably within a range of  $0.1 \leq x \leq 0.9$  at molar ratio. It is because when the content of potassium is too small, a relative dielectric constant  $\epsilon_r$ , an electromechanical coupling factor  $k_r$ , and the amount of displacement cannot be sufficiently increased, and when the content of potassium is too large, vigorous volatilization of potassium occurs during sintering, so it is difficult to perform sintering.

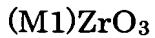
The content of lithium in the first element is preferably within a range from 0 mol% to 10 mol% inclusive. In other words, for example, the value of y in Chemical Formula 1 is preferably within a range of  $0 \leq y \leq 0.1$

at molar ratio. It is because when the content of lithium is too large, the relative dielectric constant  $\epsilon_r$ , the electromechanical coupling factor  $k_r$  and the amount of displacement cannot be sufficiently increased.

A composition ratio of the first element to the second element (the first element/the second element), that is, for example, the value of  $p$  in Chemical Formula 1 is preferably within a range of 0.95 to 1.05 inclusive at molar ratio. It is because when it is less than 0.95, the relative dielectric constant  $\epsilon_r$ , the electromechanical coupling factor  $k_r$  and the amount of displacement become smaller, and when it is larger than 1.05, polarization is difficult due to a decline in sintering density.

The second perovskite-type oxide includes a third element including at least an alkaline-earth metal element and a fourth element including at least zirconium, and oxygen. As the alkaline-earth metal element, at least one kind selected from the group consisting of magnesium, calcium, strontium and barium is preferable. It is because in such a case, superior piezoelectric properties can be obtained. The chemical formula of the second perovskite-type oxide is represented by, for example, Chemical Formula 2.

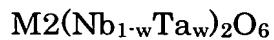
#### [Chemical Formula 2]



In the formula, M1 represents the third element. The composition ratio of the third element, the fourth element (Zr) and oxygen is stoichiometrically determined, and may deviate from the stoichiometric composition.

The tungsten bronze-type oxide includes a fifth element, a sixth element and oxygen. The fifth element preferably includes, for example, at least an alkaline-earth metal element, and more preferably includes at least one kind selected from the group consisting of magnesium, calcium, strontium and barium. The sixth element includes, for example, at least niobium, and preferably further includes tantalum. It is because in such a case, superior piezoelectric properties can be obtained by including no lead or reducing the content of lead. The chemical formula of the tungsten bronze-type oxide is represented by, for example, Chemical Formula 3.

[Chemical Formula 3]



In the formula, M<sub>2</sub> represents the fifth element, and the value of w is within a range of  $0 \leq w < 1$ . The composition ratio of the fifth element, the sixth element ( $\text{Nb}_{1-w}\text{Ta}_w$ ) and oxygen is stoichiometrically determined, and may deviate from the stoichiometric composition.

The sixth element may be the same as or different from the second element. The total content of tantalum in the second element and the sixth element is preferably 10 mol% or less. It is because when the content of tantalum is too large, the Curie temperature is decreased, and the electromechanical coupling factor kr and the amount of displacement become smaller.

A composition ratio of the first perovskite-type oxide, the second perovskite-type oxide and the tungsten bronze-type oxide is preferably within a range shown in Chemical Formula 4 at molar ratio. More

specifically, the content of the second perovskite-type oxide in the composition is preferably larger than 0 mol% and less than 10 mol%. It is because when the second perovskite-type oxide is included, the relative dielectric constant  $\epsilon_r$  and the amount of displacement can be increased; however, when the content of the second perovskite-type oxide is too large, it is difficult to perform sintering. The content of the tungsten bronze-type oxide is preferably larger than 0 mol% and equal to or less than 1 mol%. It is because when the tungsten bronze-type oxide is included, sintering can be performed more easily, and the relative dielectric constant  $\epsilon_r$ , the electromechanical coupling factor  $k_r$  and the amount of displacement can be increased; however, when the content of the tungsten bronze-type oxide is too large, the electromechanical coupling factor  $k_r$  and the amount of displacement become smaller.

#### [Chemical Formula 4]



In the formula, A represents the first perovskite-type oxide, B represents the second perovskite-type oxide, and C represents the tungsten bronze-type oxide, and the values of m and n are within a range of  $0 < m < 0.1$  and  $0 < n \leq 0.01$ , respectively.

The piezoelectric ceramic preferably includes at least one kind selected from elements of Groups 3 through 14 in the long form of the periodic table of the elements as a sub-component in addition to the above composition as the main component. It is because the piezoelectric properties can be further improved. The sub-component may exist as an

oxide in a grain boundary of the composition as the main component, or may exist by being dispersed in a part of the composition as the main component.

As the sub-component, manganese is preferably included as a first sub-component. It is because sinterability is improved, thereby the piezoelectric properties can be improved. The content of manganese as an oxide ( $MnO$ ) is preferably within a range from 0.1 wt% to 1 wt% inclusive relative to the main component. It is because the sinterability can be improved within the range.

As the sub-component, in addition to manganese, at least one kind selected from the group consisting of cobalt, iron, nickel, zinc, scandium, titanium, zirconium, hafnium, aluminum, gallium, indium, silicon, germanium and tin is preferably included as a second sub-component. It is because in addition to an improvement in sinterability, the second sub-component has a function of improving the piezoelectric properties. The total content of the second sub-component as an oxide ( $Co_3O_4$ ,  $Fe_2O_3$ ,  $NiO$ ,  $ZnO$ ,  $Sc_2O_3$ ,  $TiO_2$ ,  $ZrO_2$ ,  $HfO_2$ ,  $Al_2O_3$ ,  $Ga_2O_3$ ,  $In_2O_3$ ,  $SiO_2$ ,  $GeO_2$ ,  $SnO_2$ ) is preferably within a range of 0.01 wt% to 1 wt% inclusive relative to the main component. It is because properties can be improved within the range.

In addition, the piezoelectric ceramic may include lead (Pb), but the content of lead is preferably within a range of 1 wt% or less, and more preferably, no lead is included. It is because the volatilization of lead during sintering, and the emission of lead into environment after the

piezoelectric ceramic is distributed in a market as a piezoelectric part, and then disposed can be minimized, and it is preferable in the point of low emission, environment and ecology.

The piezoelectric ceramic is preferably used as, for example, a material of a vibration device such as an actuator, a sound component, a sensor or the like which is a piezoelectric device.

FIG. 1 shows an example of a piezoelectric device using the piezoelectric ceramic according to the embodiment. The piezoelectric device includes a piezoelectric substrate 1 made of the piezoelectric ceramic according to the embodiment, and a pair of electrodes 2 and 3 disposed on a pair of facing surfaces 1a and 1b of the piezoelectric substrate 1, respectively. The piezoelectric substrate 1 is polarized, for example, in a thickness direction, that is, a direction where the electrodes 2 and 3 face each other, and the application of a voltage through the electrodes 2 and 3 causes longitudinal vibration in a thickness direction and extensional vibration in a diameter direction.

The electrodes 2 and 3 are made of, for example, metal such as gold (Au), and are disposed on the whole facing surfaces 1a and 1b of the piezoelectric substrate 1, respectively. The electrodes 2 and 3 are electrically connected to an external power source (not shown) through a wire (not shown).

For example, the piezoelectric ceramic and the piezoelectric device having such a structure can be manufactured as follows.

FIG. 2 shows a flowchart showing a method of manufacturing the

piezoelectric ceramic. At first, as materials of the elements of the main component, for example, oxide powders including sodium, potassium, lithium, niobium, tantalum, an alkaline-earth metal element and zirconium are prepared as required. Further, as a material of the sub-component, for example, an oxide powder including at least one kind selected from elements of Groups 3 through 14 in the long form of the periodic table of the elements, for example, manganese, cobalt, iron, nickel, zinc, scandium, titanium, zirconium, hafnium, aluminum, gallium, indium, silicon, germanium and tin is prepared as required. As the materials of the main component and the sub-component, materials such as carbonates or oxalates which become oxides by sintering may be used instead of the oxides. Next, after these materials are sufficiently dried, the materials are weighed so that the final composition is within the above-described range (step S101).

Next, for example, after the materials of the second perovskite-type oxide are sufficiently mixed in an organic solvent or water by a ball mill or the like, the materials are dried, and sintered at 1000°C to 1200°C for 2 hours to 4 hours so as to form the second perovskite-type oxide (step S102).

After the second perovskite-type oxide is formed, the second perovskite-type oxide, the materials of the first perovskite-type oxide and the materials of the tungsten bronze-type oxide are sufficiently mixed in an organic solvent or water by a ball mill or the like to form a mixture. After that, the mixture is dried and press-molded, and then calcined at 750°C to 1100°C for 1 to 4 hours (step S103). As described above, the second

perovskite-type oxide is formed, and then other materials of the main component are mixed with the second perovskite-type oxide, because if the materials of the second perovskite-type oxide and the materials of the first perovskite-type oxide are mixed and sintered, the materials of the second perovskite-type oxide react with the first perovskite-type oxide, thereby the second perovskite-type oxide is not formed.

After calcining, for example, the calcined material is sufficiently pulverized by a ball mill or the like in an organic solvent or water, and is dried again, then a binder is added to the material to granulate the material. After granulating, the granulated powder is press-molded by the use of a uniaxial press, a cold isostatic press (CIP) or the like (step S104).

After molding, for example, the molded body is heated to remove the binder, and then is further sintered at 950°C to 1350°C for 2 to 4 hours (step S105). After sintering, the obtained sintered body is processed as required to form the piezoelectric substrate 1, and the electrodes 2 and 3 are disposed on the piezoelectric substrate 1, and then an electric field is applied to the piezoelectric substrate 1 in heated silicon oil to carry out polarization (step S106). Thereby, the above-described piezoelectric ceramic and the piezoelectric device shown in FIG. 1 can be obtained.

Thus, in the embodiment, the first perovskite-type oxide including sodium, potassium and niobium, the second perovskite-type oxide including an alkaline-earth metal element and zirconium and the tungsten bronze-type oxide are included, and the content of the second perovskite-type oxide in the main component is less than 10 mol%, so the relative dielectric

constant  $\epsilon_r$ , the electromechanical coupling factor  $k_r$  and the amount of displacement can be increased. Further, sintering can be easily performed.

Therefore, availability of the piezoelectric ceramic and the piezoelectric device including no lead or a smaller content of lead can be increased. In other words, the volatilization of lead during sintering is reduced, and the risk of emitting lead into environment is lower even after the piezoelectric ceramic and the piezoelectric device are distributed in a market and then disposed, so the piezoelectric ceramic and the piezoelectric device being superior in the point of low emission, environment and ecology can be utilized.

More specifically, when the content of potassium in the first element is within a range of 10 mol% to 90 mol% inclusive, superior piezoelectric properties can be obtained, and sintering can be more easily performed.

Moreover, when 10 mol% or less of lithium is included as the first element, or when the composition ratio of the first element to the second element (the first element/the second element) is within a range from 0.95 to 1.05 inclusive at molar ratio, the relative dielectric constant  $\epsilon_r$ , the electromechanical coupling factor  $k_r$  and the amount of displacement can be further increased.

Further, when the content of the tungsten bronze-type oxide in the composition is within a range of 1 mol% or less, the electromechanical coupling factor  $k_r$  and the amount of displacement can be further increased.

In addition, when the tungsten bronze-type oxide includes the fifth element including an alkaline-earth metal element, the sixth element

including at least niobium selected from the group consisting of niobium and tantalum, and oxygen, and specifically when the fifth element includes at least one kind selected from the group consisting of magnesium, calcium, strontium and barium, superior piezoelectric properties can be obtained.

Moreover, when the total content of tantalum in the second element and the sixth element is within a range of 10 mol% or less, the electromechanical coupling factor kr and the amount of displacement can be further increased.

Further, when at least one kind selected from elements of Groups 3 through 14 in the long form of the periodic table of the elements is included as the sub-component, the piezoelectric properties can be further improved. In particular, when manganese as an oxide is included within a range from 0.1 wt% to 1 wt% inclusive relative to the main component as the first sub-component, sinterability is improved, thereby the piezoelectric properties can be improved. Further, when, in addition to manganese, at least one kind selected from the group consisting of cobalt, iron, nickel, zinc, scandium, titanium, zirconium, hafnium, aluminum, gallium, indium, silicon, germanium and tin as an oxide is included as the second sub-component within a range from 0.01 wt% to 1 wt% inclusive relative to the main component in total, the piezoelectric properties can be further improved.

In addition, when the second perovskite-type oxide, the materials of the elements of the first perovskite-type oxide and the materials of the elements of the tungsten bronze-type oxide are mixed, calcined and

sintered, the piezoelectric ceramic according to the embodiment can be easily obtained, and the piezoelectric ceramic according to the embodiment can be achieved.

**Examples]**

Next, specific examples of the invention will be described below.

**(Examples 1·1, 1·2)**

A piezoelectric ceramic including, as a main component, a composition represented by Chemical Formula 5 which included the first perovskite-type oxide, the second perovskite-type oxide and the tungsten bronze-type oxide was used to form a piezoelectric device shown in FIG. 1 through the steps shown in FIG. 2. Examples 1·1 and 1·2 will be described referring to FIGs. 1 and 2 using numerals shown in FIG. 1.

**[Chemical Formula 5]**



At first, as materials of the main component, a sodium carbonate ( $Na_2CO_3$ ) powder, a potassium carbonate ( $K_2CO_3$ ) powder, a lithium carbonate ( $Li_2CO_3$ ) powder, a niobium oxide ( $Nb_2O_5$ ) powder, a strontium carbonate ( $SrCO_3$ ) powder, a zirconium oxide ( $ZrO_2$ ) powder and a barium carbonate ( $BaCO_3$ ) powder were prepared. Moreover, as a material of the sub-component, a manganese carbonate ( $MnCO_3$ ) powder was prepared. Next, after the materials of the main component and the sub-component were sufficiently dried, they were weighed so that the main component became the composition shown in Chemical Formula 5 and Table 1, and the content of manganese which was the sub-component as an oxide was 0.31

wt% relative to the main component (refer to step S101 in FIG. 2). The weights of the carbonates among the materials of the main component were calculated as oxides formed through dissociating CO<sub>2</sub> from the carbonates, and as the content of the sub-component, the amount of the mixed manganese carbonate powder which was the material of the sub-component was 0.5 wt% relative to the total weight of the materials of the main component.

[Table 1]

	COMPOSITION OF MAIN COMPONENT m(mol)	CONTENT OF SUB-COMPONENT Mn * (WT%)	RELATIVE DIELECTRIC CONSTANT $\epsilon_r$	ELECTROMECHANICAL COUPLING FACTOR Kr (%)	AMOUNT OF DISPLACEMENT (%)
EXAMPLE 1-1	0.005	0.31	737	38.2	0.086
EXAMPLE 1-2	0.01	0.31	889	40.4	0.100
COMPARATIVE EXAMPLE 1-1	0	0.31	535	43.1	0.083
COMPARATIVE EXAMPLE 1-2	0.1	0.31	—	—	—

\* The content of the sub-component is a value as an oxide (MnO) relative to the main component.

Next, after the strontium carbonate powder and the zirconium powder were mixed in water by a ball mill, and dried, the mixture was sintered at 1100°C for 2 hours so as to form strontium zirconate as the second perovskite-type oxide (refer to step S102 in FIG. 2).

After strontium zirconate was formed, strontium zirconate, other materials of the main component and the materials of the sub-component were mixed in water by a ball mill, dried, press-molded and calcined for 2 hours at 850°C to 1000°C (refer to step S103 in FIG. 2). After calcining, the calcined body was pulverized by a ball mill in water, and was dried again,

and then polyvinyl alcohol was added to the body to granulate the body. After granulating, the granulated powder was molded by the use of a uniaxial press at a pressure of approximately 40 MPa so as to form a disk-shaped pellet with a diameter of 17 mm (refer to step S104 in FIG. 2).

After molding, the molded body was heated for 4 hours at 650°C to remove the binder, and then the molded body was further sintered at 950°C to 1350°C for 4 hours (refer to step S105 in FIG. 2). After that, the sintered body was processed into a disk shape with a thickness of 0.6 mm so as to form the piezoelectric substrate 1, and a silver paste was printed on both sides of the piezoelectric substrate 1, and baked at 650°C so as to form the electrodes 2 and 3. After forming the electrodes 2 and 3, an electric field of 3 kV/mm to 10 kV/mm was applied to the piezoelectric substrate 1 in silicon oil of 30°C to 250°C for 1 to 30 minutes to carry out polarization (refer to step S106 in FIG. 2). Thereby, the piezoelectric devices of Examples 1·1 and 1·2 were obtained.

After the obtained piezoelectric devices of Examples 1·1 and 1·2 were left alone for 24 hours, as the piezoelectric properties, the relative dielectric constant  $\epsilon_r$ , the electromechanical coupling factor  $k_r$ , and the amount of displacement in the case where an electric field of 3 kV/mm was applied were measured. The relative dielectric constant  $\epsilon_r$  and the electromechanical coupling factor  $k_r$  were measured by an impedance analyzer (Hewlett-Packard's HP4194A), and a frequency when measuring the relative dielectric constant  $\epsilon_r$  was 1 kHz. The amount of displacement was measured by a displacement measuring device using eddy currents as

shown in FIG. 3. In the displacement measuring device, a test sample 13 was sandwiched between a pair of electrodes 11 and 12, and the displacement of the test sample 13 when a direct current was applied was detected by a displacement sensor 14, and then the amount of displacement was determined by a displacement detector 15. These results are shown in Table 1. The amount of displacement shown in Table 1 was determined by dividing the measured value by the thickness of the test sample and then multiplying by 100 (the measured value/the thickness of the test sample × 100).

As Comparative Example 1·1 relative to the examples, a piezoelectric device was formed as in the case of Examples 1·1 and 1·2, except that strontium zirconate as the second perovskite-type oxide was not included, that is, the value of m in Chemical Formula 5 was 0. Moreover, as Comparative Example 1·2 relative to the examples, a piezoelectric device was formed as in the case of Examples 1·1 and 1·2, except that the content of strontium zirconate in the main component was 10 mol%, that is, the value of m in Chemical Formula 5 was 0.1. The content of the sub-component was the same as that in Examples 1·1 and 1·2.

The relative dielectric constant  $\epsilon_r$ , the electromechanical coupling factor kr and the amount of displacement in the case where an electric field of 3 kV/mm was applied in the piezoelectric devices of Comparative Examples 1·1 and 1·2 were measured as in the case of Examples 1·1 and 1·2. These results are also shown in Table 1.

As shown in Table 1, Examples 1·1 and 1·2 could obtain higher

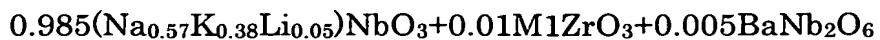
values of the relative dielectric constant  $\epsilon_r$  and the amount of displacement than those in Comparative Example 1-1 in which no strontium zirconate was included. Moreover, there was a tendency that as the value of m in Chemical Formula 5 increased, that is, as the content of strontium zirconate increased, the relative dielectric constant  $\epsilon_r$  and the amount of displacement increased. Further, in Comparative Example 1-2 in which the content of strontium zirconate was 10 mol%, sintering could not be performed, thereby the properties could not be measured.

In other words, it was clear that when the second perovskite-type oxide was included within a range of less than 10 mol% in the main component in addition to the first perovskite-type oxide and the tungsten bronze-type oxide, the amount of displacement could be increased.

(Examples 1-3 to 1-5)

Piezoelectric devices of Examples 1-3 through 1-5 were formed as in the case of Example 1-2, except that a composition shown in Chemical Formula 6 was included as the main component. At that time, in Examples 1-3 through 1-5, the third element (M1 in Chemical Formula 6) was changed as shown in Table 2. As the materials of magnesium, calcium and barium, a basic manganese carbonate ( $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ ) powder, a calcium carbonate ( $\text{CaCO}_3$ ) powder and a barium carbonate powder were used. The content of the sub-component was the same as that in Example 1-2.

[Chemical Formula 6]



[Table 2]

	COMPOSITION OF MAIN COMPONENT M <sub>1</sub>	CONTENT OF SUB-COMPONENT Mn * (WT%)	RELATIVE DIELECTRIC CONSTANT $\epsilon_r$	ELECTROMECHANICAL COUPLING FACTOR K <sub>r</sub> (%)	AMOUNT OF DISPLACEMENT (%)
EXAMPLE 1-2	Sr	0.31	889	40.4	0.100
EXAMPLE 1-3	Mg	0.31	791	37.2	0.087
EXAMPLE 1-4	Ca	0.31	852	38.0	0.092
EXAMPLE 1-5	Ba	0.31	820	37.9	0.090
COMPARATIVE EXAMPLE 1-1	—	0.31	535	43.1	0.083

\* The content of the sub-component is a value as an oxide (MnO) relative to the main component.

The relative dielectric constant  $\epsilon_r$ , the electromechanical coupling factor kr and the amount of displacement in the case where an electric field of 3 kV/mm was applied in the piezoelectric devices of Examples 1-3 through 1-5 were measured as in the case of Example 1-2. The results are shown in Table 2 together with the results of Example 1-2 and Comparative Example 1-1.

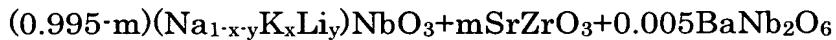
As shown in Table 2, as in the case of Example 1-2, Examples 1-3 through 1-5 could obtain higher values of relative dielectric constant  $\epsilon_r$  and the amount of displacement. In other words, it was clear that even if the third element was changed, the piezoelectric properties could be improved, and the amount of displacement could be increased.

(Examples 2-1 to 2-7)

Piezoelectric devices were formed as in the case of Examples 1-1 and 1-2, except that a composition shown in Chemical Formula 7 was included as the main component. At that time, in Examples 2-1 through 2-7, the composition of the first element (the values of x and y in Chemical

Formula 7) and the content of strontium zirconate as the second perovskite-type oxide (the value of m in Chemical Formula 7) were changed as shown in Table 3. The content of the sub-component was the same as that in Examples 1-1 and 1-2.

[Chemical Formula 7]



[Table 3]

	COMPOSITION OF MAIN COMPONENT			CONTENT OF SUB-COMPONENT Mn * (WT%)	RELATIVE DIELECTRIC CONSTANT $\epsilon_r$	ELECTROMECHANICAL COUPLING FACTOR Kr (%)	AMOUNT OF DISPLACEMENT (%)
	x (mol)	y (mol)	m (mol)				
EXAMPLE 2-1	0.19	0.05	0.08	0.31	583	26.7	0.054
EXAMPLE 2-2	0.285	0.05	0.01	0.31	536	34.1	0.066
EXAMPLE 2-3	0.285	0.05	0.02	0.31	766	34.5	0.079
EXAMPLE 2-4	0.36	0.1	0.01	0.31	1211	33.3	0.096
EXAMPLE 2-5	0.75	0.05	0.03	0.31	620	30.4	0.063
EXAMPLE 2-6	0.6	0	0.01	0.31	429	40.6	0.070
EXAMPLE 2-7	0.8	0	0.08	0.31	507	25.5	0.048
COMPARATIVE EXAMPLE 2-1	0.19	0.05	0	0.31	348	30.5	0.048
COMPARATIVE EXAMPLE 2-2	0.285	0.05	0	0.31	344	34.8	0.052
COMPARATIVE EXAMPLE 2-3	0.36	0.1	0	0.31	763	34.3	0.080
COMPARATIVE EXAMPLE 2-4	0.75	0.05	0	0.31	374	32.2	0.053
COMPARATIVE EXAMPLE 2-5	0.6	0	0	0.31	270	42.8	0.058
COMPARATIVE EXAMPLE 2-6	0.8	0	0	0.31	239	29.2	0.040

\* The content of the sub-component is a value as an oxide (MnO) relative to the main component.

As Comparative Examples 2-1 through 2-6 relative to the examples, piezoelectric devices were formed as in the case of Examples 2-1 through 2-7, except that strontium zirconate as the second perovskite-type oxide was not included. Comparative Examples 2-1, 2-2, 2-3, 2-4, 2-5, and 2-6 correspond to Examples 2-1, 2-2 and 2-3, 2-4, 2-5, 2-6, and 2-7, respectively.

The relative dielectric constant  $\epsilon_r$ , the electromechanical coupling factor  $kr$  and the amount of displacement in the case where an electric field of 3 kV/mm was applied in the piezoelectric devices of Examples 2·1 through 2·7 and Comparative Examples 2·1 through 2·6 were measured as in the case of Examples 1·1 and 1·2. The results are shown in Table 3.

As shown in Table 3, as in the case of Examples 1·1 and 1·2, Examples 2·1 through 2·7 could obtain higher values of relative dielectric constant  $\epsilon_r$  and the amount of displacement than those in the comparative examples. Moreover, there was a tendency that as the value  $x$  in Chemical Formula 7 increased, that is, as the content of potassium increased, the relative dielectric constant  $\epsilon_r$ , the electromechanical coupling factor  $kr$  and the amount of displacement were increased to the maximum values, then decreased. In other words, it was clear that when the content of potassium in the first element was within a range from 10 mol% to 90 mol% inclusive, the piezoelectric properties could be improved, and the amount of displacement could be increased.

Moreover, there was a tendency that when lithium was included as the first element, the relative dielectric constant  $\epsilon_r$ , the electromechanical coupling factor  $kr$  and the amount of displacement were further increased. In other words, it was clear that when 10 mol% or less of lithium was included in the first element, the piezoelectric properties could be improved, and the amount of displacement could be increased.

(Examples 3·1, 3·2)

Piezoelectric devices were formed as in the case of Examples 1·1

and 1·2, except that a composition shown in Chemical Formula 8 was included as the main component. At that time, in Examples 3·1 and 3·2, the content of tantalum (the values of z and w in Chemical Formula 8) and the content of strontium zirconate as the second perovskite-type oxide (the value of m in Chemical Formula 8) were changed as shown in Table 4. The content of the sub-component was the same as that in Examples 1·1 and 1·2, and a tantalum oxide ( $Ta_2O_5$ ) powder was used as the material of tantalum.

[Chemical Formula 8]



[Table 4]

	COMPOSITION OF MAIN COMPONENT		CONTENT OF SUB-COMPONENT Mn * (WT%)	RELATIVE DIELECTRIC CONSTANT $\epsilon_r$	ELECTROMECHANICAL COUPLING FACTOR Kr (%)	AMOUNT OF DISPLACEMENT (%)
	z,w (mol)	m (mol)				
EXAMPLE 1·1	0	0.005	0.31	737	38.2	0.086
EXAMPLE 1·2	0	0.01	0.31	889	40.4	0.100
EXAMPLE 3·1	0.05	0.005	0.31	912	41.4	0.104
EXAMPLE 3·2	0.05	0.01	0.31	1108	43.6	0.120
COMPARATIVE EXAMPLE 1·1	0	0	0.31	535	43.1	0.083
COMPARATIVE EXAMPLE 3·1	0.05	0	0.31	883	42.0	0.101

\* The content of the sub-component is a value as an oxide (MnO) relative to the main component.

As Comparative Example 3·1 relative to the examples, a piezoelectric device was formed as in the case of Examples 3·1 and 3·2, except that strontium zirconate as the second perovskite-type oxide was not included. The relative dielectric constant  $\epsilon_r$ , the electromechanical

coupling factor  $k_r$  and the amount of displacement in the case where an electric field of 3 kV/mm was applied in the piezoelectric devices of Examples 3·1 and 3·2 and Comparative Example 3·1 were measured as in the case of Examples 1·1 and 1·2. The results are shown in Table 4 together with the results of Examples 1·1 and 1·2 and Comparative Example 1·1.

As shown in Table 4, as in the case of Examples 1·1 and 1·2, Examples 3·1 and 3·2 could obtain higher values of relative dielectric constant  $\epsilon_r$  and the amount of displacement than those in Comparative Example 3·1. Moreover, Examples 3·1 and 3·2 in which tantalum was included in the second element and the sixth element could obtain a larger amount of displacement than that in Examples 1·1 and 1·2 in which tantalum was not included.

In other words, it was clear that when tantalum was included in the second element or the sixth element, the amount of displacement could be increased.

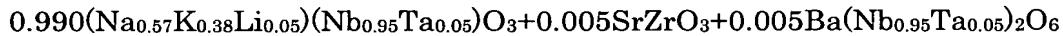
In the examples, the case where the contents of tantalum in the second element and the sixth element, that is, the values of  $z$  and  $w$  in Chemical Formula 8 are the same is shown; however, even in the case where the values of  $z$  and  $w$  are different, the same effects can be obtained.

(Examples 4·1 to 4·3, 5·1 to 5·13)

Piezoelectric devices were formed as in the case of Example 3·1, except that a composition shown in Chemical Formula 9 as the main component was included, and a sub-component shown in Table 5 or 6 was

added. As the material of the second sub-component, a cobalt oxide ( $\text{Co}_3\text{O}_4$ ) powder, an iron oxide ( $\text{Fe}_2\text{O}_3$ ) powder, a nickel oxide ( $\text{NiO}$ ) powder, a zinc oxide ( $\text{ZnO}$ ) powder, a scandium oxide ( $\text{Sc}_2\text{O}_3$ ) powder, a titanium oxide ( $\text{TiO}_2$ ) powder, a zirconium oxide ( $\text{ZrO}_2$ ) powder, a hafnium oxide ( $\text{HfO}_2$ ) powder, an aluminum oxide ( $\text{Al}_2\text{O}_3$ ) powder, a gallium oxide ( $\text{Ga}_2\text{O}_3$ ) powder, an indium oxide ( $\text{In}_2\text{O}_3$ ) powder, a silicon oxide ( $\text{SiO}_2$ ) powder, a germanium oxide ( $\text{GeO}_2$ ) powder or a tin oxide ( $\text{SnO}_2$ ) powder was used. The content of the sub-component shown in Table 5 or 6 was a value as an oxide ( $\text{MnO}$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{ZnO}$ ,  $\text{Sc}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{HfO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{GeO}_2$ ,  $\text{SnO}_2$ ) relative to the main component.

[Chemical Formula 9]



[Table 5]

	CONTENT OF FIRST SUB-COMPONENT* (WT%)	SECOND SUB-COMPONENT		RELATIVE DIELECTRIC CONSTANT $\epsilon_r$	ELECTROMECHANICAL COUPLING FACTOR Kr (%)	AMOUNT OF DISPLACEMENT (%)
		ELEMENT	CONTENT* (WT%)			
EXAMPLE 3-1	0.31	—	0	912	41.4	0.104
EXAMPLE 4-1	0.31	Co	0.01	922	43.2	0.109
EXAMPLE 4-2	0.31	Co	0.2	944	47.2	0.120
EXAMPLE 4-3	0.31	Co	1	905	44.1	0.110

\* The content is a value as an oxide ( $\text{MnO}$ ) relative to the main component.

[Table 6]

	CONTENT OF FIRST SUB-COMPONENT* (WT%)	SECOND SUB-COMPONENT		RELATIVE DIELECTRIC CONSTANT $\epsilon_r$	ELECTROMECHANICAL COUPLING FACTOR Kr (%)	AMOUNT OF DISPLACEMENT (%)
		ELEMENT	CONTENT* (WT%)			
EXAMPLE 3-1	0.31	—	0	912	41.4	0.104
EXAMPLE 4-2	0.31	Co	0.2	944	47.2	0.120
EXAMPLE 5-1	0.31	Fe	0.2	943	44.5	0.113
EXAMPLE 5-2	0.31	Ni	0.2	929	44.8	0.113
EXAMPLE 5-3	0.31	Zn	0.2	948	46.1	0.118
EXAMPLE 5-4	0.31	Sc	0.2	979	45.1	0.117
EXAMPLE 5-5	0.31	Ti	0.2	1117	42.3	0.117
EXAMPLE 5-6	0.31	Zr	0.2	1200	40.8	0.117
EXAMPLE 5-7	0.31	Hf	0.2	1060	43.2	0.117
EXAMPLE 5-8	0.31	Al	0.2	1038	41.2	0.110
EXAMPLE 5-9	0.31	Ga	0.2	1116	41.5	0.115
EXAMPLE 5-10	0.31	In	0.2	1055	41.1	0.111
EXAMPLE 5-11	0.31	Si	0.2	1028	40.3	0.107
EXAMPLE 5-12	0.31	Ge	0.2	1100	43.4	0.119
EXAMPLE 5-13	0.31	Sn	0.2	1050	42.0	0.113

\* The content is a value as an oxide (MnO) relative to the main component.

The relative dielectric constant  $\epsilon_r$ , the electromechanical coupling factor kr and the amount of displacement in the case where an electric field of 3 kV/mm was applied in the piezoelectric devices of Examples 4-1 through 4-3 and Examples 5-1 through 5-13 were measured as in the case of Examples 1-1 and 1-2. The results are shown in Tables 5 and 6 together with the results of Example 3-1.

As shown in Table 5, in Examples 4-1 through 4-3 in which cobalt was added as the second sub-component, a larger amount of displacement

than that in Example 3-1 in which the second sub-component was not included was obtained. Moreover, it was obvious from a comparison between Examples 4-1 through 4-3 that there was a tendency that when the content of cobalt as the second sub-component increased, the amount of displacement increased to the maximum value, then decreased.

Further, as shown in Table 6, when iron, nickel, zinc, scandium, titanium, zirconium, hafnium, aluminum, gallium, indium, silicon, germanium or tin was included as the second sub-component, as in the case where cobalt was included, an improvement in the amount of displacement was observed.

In other words, it was clear that when at least one kind selected from the group consisting of cobalt, iron, nickel, zinc, scandium, titanium, zirconium, hafnium, aluminum, gallium, indium, silicon, germanium and tin was included as the second sub-component, the piezoelectric properties could be further improved. Moreover, it was clear that the total content of the second sub-component as an oxide was preferably within a range from 0.01 wt% to 1 wt% inclusive relative to the main component.

In the above examples, some compositions including the first perovskite-type oxide, the second perovskite-type oxide and the tungsten bronze-type oxide are described as examples in detail. However, as long as a composition is within a range described in the above embodiment, the same effects can be obtained.

Although the present invention is described referring to the embodiment and the examples, the invention is not limited to the above

embodiment and the above examples, and is variously modified. For example, in the above embodiment and the above examples, the case where the composition including the first perovskite-type oxide, the second perovskite-type oxide and the tungsten bronze-type oxide is included is described; however, any other component may be further included in the composition in addition to the first perovskite-type oxide, the second perovskite-type oxide and the tungsten bronze-type oxide.

Moreover, in the above embodiment and the examples, the case where the composition of the main component includes at least sodium and potassium selected from the group consisting of sodium, potassium and lithium as the first element, at least niobium selected from the group consisting of niobium and tantalum as the second element, at least one kind selected from alkaline-earth metal elements as the third element, at least titanium as the fourth element, at least one kind selected from alkaline-earth metal elements as the fifth element, and at least niobium selected from the group consisting of niobium and tantalum as the sixth element is described; however, each of the first element, the second element, the third element, the fourth element, the fifth element and the sixth element may further include any other element.

Further, in the above embodiment and the examples, the case where the sub-component is included in addition to the composition of the main component is described; however, as long as the composition of the main component is included, the invention can be widely applied to the case where the sub-component is not included. Further, the invention can

be applied to the case where any other sub-component is included in a like manner.

In addition, in the above embodiment, although the piezoelectric device with a single-layer structure is described, the invention can be applied to a piezoelectric device with any other structure such as a multilayer structure in a like manner. Further, although a vibration device such as an actuator, a sound component and a sensor are taken as examples of the piezoelectric device, the invention can be applied to any other piezoelectric device.

#### **INDUSTRIAL APPLICABILITY**

The piezoelectric ceramic can be used in piezoelectric devices including vibration device such as actuators, sound components and sensors.